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# <Division of Synthetic Chemistry>Organoelement Chemistry

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# Division of Synthetic Chemistry – Organoelement Chemistry –

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## Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of “dreams” for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry.

### KEYWORDS

Steric Protection    Kinetic Stabilization    Low-coordinated Species  
Heteroatom          Transition Metal Complexes



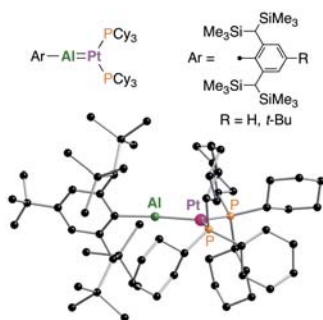
## Selected Publications

Wasano, T.; Agou, T.; Sasamori, T.; Tokitoh, N., Synthesis, Structure and Reactivity of a 1-Bromoalumole, *Chem. Commun.*, **50**, 8148-8150 (2014).  
Agou, T.; Nagata, K.; Sasamori, T.; Tokitoh, N., Reaction of a Dialumene-Benzene Adduct with Diphenylacetylene: Formation of 3,4-Dialuminacyclobutene and 5,6-Dialuminabicyclo[2.1.1]hex-2-ene Derivatives, *Chem. Asian. J.*, **9**, 3099-3101 (2014).  
Agou, T.; Hayakawa, N.; Sasamori, T.; Matsuo, T.; Hashizume, D.; Tokitoh, N., Reactions of Diaryldibromodisilenes with *N*-Heterocyclic Carbenes: Formation of Formal Bis-NHC Adducts of Silyliumylidene Cations, *Chem. Eur. J.*, **20**, 9246-9249 (2014).  
Nagata, K.; Agou, T.; Tokitoh, N., Syntheses and Structures of Terminal Arylalumylene Complexes, *Angew. Chem. Int. Ed.*, **53**, 3881-3884 (2014).  
Tsurusaki, A.; Sasamori, T.; Tokitoh, N., Synthesis and Structure of a 1-Phospha-2-boraacenaphthene Derivative and Its Chalcogenation Reactions, *Chem. Eur. J.*, **20**, 3752-3758 (2014).  
Matsumoto, T.; Sasamori, T.; Miyake, H.; Tokitoh, N., Synthesis of a Rhodium Carbonyl Phosphaalkenyl-Phosphido Complex: A Phosphorus Congener of Schiff Base Type *N,N'*-Chelating Monoanionic Ligands, *Organometallics*, **33**, 1341-1344 (2014).

## Terminal Arylalumylene Complexes

Group 13 element (B, Al, Ga, In, and Tl) compounds have less than an octet and have tendency to form an octet by accepting an electron pair from a Lewis base. Therefore, it is difficult to construct  $\pi$ -electron systems (multiple bond,  $\pi$ -conjugated system, and so on) containing a Group 13 element with keeping the vacant p-orbital. Especially, there had been few reports on the Al-containing  $\pi$ -electron systems. We have already succeeded in the synthesis of a benzene-adduct of dialumene (an Al–Al double-bond compound) and revealed its synthetic equivalency to dialumene. During the course of our studies on the reactivity of dialumene-benzene adducts, we have succeeded in the synthesis of novel platinum complexes of terminal aluminyls (monovalent aluminum species).

Terminal arylaluminylene complexes of platinum [ArAl–Pt(PCy<sub>3</sub>)<sub>2</sub>] [Ar = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (Bbp) or 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-(*t*-Bu)C<sub>6</sub>H<sub>2</sub> (Tbb)] have been synthesized either by the reaction of a dialumene-benzene adduct with [Pt(PCy<sub>3</sub>)<sub>2</sub>]. X-Ray crystallographic analysis (Figure 1) revealed that the Al–Pt bond lengths of these arylaluminylene complexes are shorter than the shortest Al–Pt distance reported previously. DFT calculations suggest that the Al–Pt bonds in the arylaluminylene complexes have a significantly high electrostatic character.



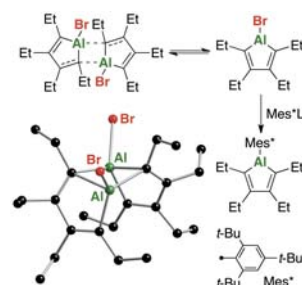
**Figure 1.** Terminal aluminylene complexes.

## 1-Bromoalumole

Heteroles of electron-deficient group 13 elements are expected to have low-lying LUMOs owing to the orbital interactions between the empty p orbital of group 13 elements and the  $\pi^*$  orbitals. Quite recently, we have succeeded in the synthesis of the first Lewis base-free alumole by the introduction of bulky substituent, Mes\* [Mes\* = 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]. DFT calculations revealed that the 3p(Al)– $\pi^*$  conjugation effectively lowers the LUMO energy level of the alumole. In order to elucidate the properties of alumoles extensively and to utilize them as the key components of functional materials, facile and versatile synthetic methods of alumoles bearing various functional

groups should be of importance. Therefore, we examined the synthesis of alumoles bearing halogen-substituent on the aluminum atom.

A stable 1-bromoalumole has been synthesized by the reaction of a 1,4-dilithio-1,3-butadiene derivative with AlBr<sub>3</sub>. The 1-bromoalumole was found to exist as a dimeric structure in the crystalline state (Figure 2). Reaction of the 1-bromoalumole with Mes\*Li afforded the corresponding Mes\*-substituted alumole, demonstrating the potential of the 1-bromoalumole for the functionalization of alumoles.

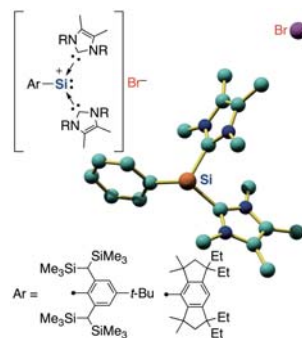


**Figure 2.** Reactivity of the 1-bromoalumole and its dimeric structure in the crystalline state.

## Bis-NHC Adducts of Silyliumylidene Cations

Silyliumylidene cation (R<sub>3</sub>Si<sup>+</sup>) is highly coordinatively-unsaturated silicon species and is one of the most challenging intermediates in silicon chemistry. Although several examples of Lewis base-coordinated silyliumylidene have been reported, we have found a novel method to access silyliumylidene stabilized by *N*-heterocyclic carbenes (NHC) by using 1,2-dibromodisilenes as starting materials.

Reactions of stable 1,2-dibromodisilenes [(*E*)-Ar(Br)Si=Si(Br)Ar] with NHC afforded NHC-arylbromosilylene [Ar(Br)Si:] adducts or bromide salts of the corresponding bis-NHC adducts of the formal arylsilyliumylidene cations ([ArSi:]<sup>+</sup>) (Figure 3). In some cases, an NHC was able to replace a bromide anion in the coordination sphere of the arylbromosilylene-NHC adduct. X-Ray crystallographic analysis revealed that the silicon centers of the bis-NHC adducts of the silyliumylidene cations possess pyramidal geometries, indicating that the lone pair electrons are substantially localized on the silicon atoms.



**Figure 3.** Bis-NHC adducts of silyliumylidene cations.